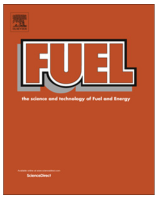
Fuel 191 (2017) 212–220

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Full Length Article

Pre-formulation of biofuels: Kinematic viscosities, low-temperature phase behaviour and nanostructuring of ethanol/“ethanolotrope”/rapeseed oil mixtures

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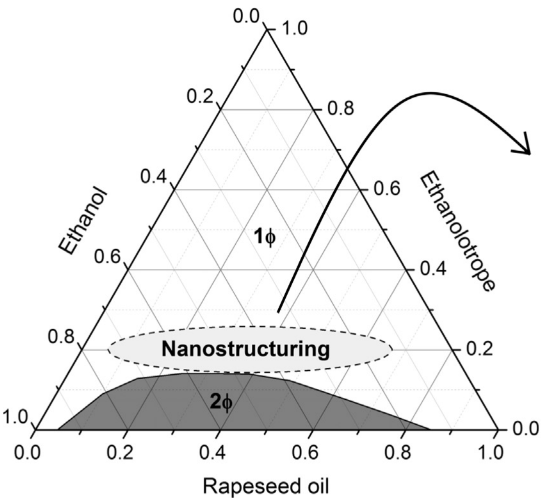
HIGHLIGHTS

- Ethanol/rapeseed oil/green additive mixtures are studied using phase diagrams.
- The temperature dependence of the kinematic viscosity and phase behaviour is studied.
- Dynamic light scattering is performed to detect the highest scattering intensity.
- The critical points and their temperature dependences are investigated.
- A correlation of the viscosity with the nanostructuring of the mixture is postulated.

GRAPHICAL ABSTRACT



Impact on fuel properties:

- Kinematic viscosity
- Low-temperature performance
- Phase behaviour

ARTICLE INFO

Article history:
Received 11 August 2016
Received in revised form 14 November 2016
Accepted 21 November 2016

Keywords:
Biofuel
“Ethanolotrope”
Kinematic viscosity
Low-temperature phase behaviour
Scattering intensity
Nanostructure

ABSTRACT

As ethanol and rapeseed oil are not miscible, tributyl citrate, 2,5-dimethylfuran (DMF), 2-methylfuran (2-MF), 2-methyltetrahydrofuran (2-MTHF), methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), rapeseed oil FAME-biodiesel (FAME), 1-heptanol (HepOH) and 2-ethylhexyl nitrate (EHN) are used as green mixing agents or “ethanolotropes”. The area of existence of clear and monophasic mixtures as well as biphasic liquid/liquid solutions, determined in a previous work, are reported at 25 °C using ternary phase diagrams. In the present work, some of these ternary diagrams are completed by investigating their critical points (CPs). Further, the kinematic viscosity (kV) of different binary and ternary, clear and monophasic mixtures is measured at 25 and 40 °C and their phase behaviour is studied at 0, −15 and −20 °C. Dynamic light scattering (DLS) experiments are performed on various samples at 25 °C and the results are discussed with respect to previous measurements including DLS, static light scattering (SLS), small and wide angle X-ray scattering (SWAXS) and conductivity. Close to the CP of the investigated systems, the highest scattering intensities (SIs) can be observed as well as a distinct increase of the slope

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Abbreviations: ASTM, American Society for Testing and Materials; CP, critical point; DLS, Dynamic light scattering; DMF, 2,5-dimethylfuran; ETBE, ethyl tert-butyl ether; EHN, 2-ethylhexyl nitrate; FAME, atty acid methyl ester derived by rapeseed oil; HepOH, 1-heptanol; HLB, Hydrophilic-lipophilic balance; kV, kinematic viscosity; 2-MF, 2-methylfuran; 2-MTHF, 2-methyltetrahydrofuran; MTBE, methyl tert-butyl ether; SI, scattering intensity; SWAXS, small and wide angle X-ray scattering; TBC, tributyl citrate.

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http://dx.doi.org/10.1016/j.fuel.2016.11.075

of the kV versus the rapeseed oil concentration. Evaluating these results, the high viscosities can be associated with the formation of a rapeseed oil continuum. Further, the monophasic domain close to the CP can be considered as bicontinuous-like. For every used "ethanolotrope", the mixtures meet the required ASTM D6751 standard for the kV of biodiesel. Thus, rules for possible adjustments to reach this standard by varying the nature and the quantities of the "ethanolotropes" are proposed. Ternary and binary melts with high amounts of rapeseed oil can meet the kV standard and are clear and monophasic below 0 °C or even below −15 °C. Binary mixtures of DMF or 2-MF with high amounts of rapeseed oil (70 wt%) show no phase transitions during several hours at −20 °C and form reversible, monophasic and clear gels. As the kV of these two binary mixtures is slightly above 6 mm^2/s at 40 °C, they nearly meet the kV standard. Replacing ethanol by "ethanolotropes" like 2-MTHF or HepOH can lead to an increase of the monophasic region of these ternary mixtures at low temperatures. Moreover, this temperature dependence could be associated with the nanostructuring, since mixtures located in the bicontinuous-like regions seem to be more sensitive regarding their phase behaviour.

1. Introduction

In the recent decades, the unstable and unpredictable prices of petroleum fuels, the uncertainties in their supply and the global warming problems caused by their continuous usage have raised the interest in biofuels. Many researchers have studied the use of vegetable oils as alternative fuel for diesel engines [1–9]. From the environmental point of view, biomass fuels such as vegetable oils, biodiesel and bioethanol can help solving global warming and environmental pollution problems due to their renewability and the absence of any sulfur, aromatic hydrocarbons and metals [1,10,11]. However, the direct use of vegetable oils in engines is limited by some physicochemical and chemical properties such as their high viscosity, low volatility and polyunsaturated nature [10,12]. The large molecular size of the triglycerides occurring in vegetable oils leads to a higher viscosity, higher density and lower volatility compared to diesel fuel. Higher viscosity causes a bad flow behaviour of the fuel in the engine, inferior fuel atomisation and poor spray behaviour from the injector [13]. Consequently, before using vegetable oil mixtures as fuel, their viscosity has to be lowered. Without reducing the viscosity, the use of vegetable oils can cause environmental problems because of their incomplete combustion [4,13].

In the present work, rapeseed oil is evaluated as a replacement for diesel fuel. Ethanol, known as a common additive for biofuels, can be envisaged to reduce the high kinematic viscosity (kV) of rapeseed oil [13,14]. However, ethanol is not miscible with rapeseed oil. Organic substances can help to co-solubilise ethanol and rapeseed oil if they are miscible with ethanol and rapeseed oil. The term "ethanolotrope" can be applied to name these molecules. Analogous to hydrotropes, they increase the solubility of rapeseed oil in ethanol, while hydrotropes enhance the solubility of organic compounds in water [15]. We decided to use methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE) as "ethanolotropes", because they are already used as gasoline and diesel additives respectively [16,17]. 2-Ethylhexyl nitrate (EHN) was selected, as it is a well-known cetane improver. Tributyl citrate (TBC), 2,5-dimethylfuran (DMF), 2-methylfuran (2-MF), 2-methyltetrahydrofuran (2-MTHF), fatty acid methyl ester (FAME) biodiesel derived from rapeseed oil and 1-heptanol (HepOH) are used in the present study, since they are obtained from biomass or the oleo industry and were already envisaged as biofuels [18–22]. The chemical structures of some "ethanolotropes" used in this study are represented in Table 1. The chemical structure of FAME is not shown because of the large variety of molecules present in this compound. FAME is constituted by a large panel of fatty acids present in rapeseed oil esterified with methanol. Taking R-COOH as general chemical structure for the fatty acid, where R represents the alkyl or alkene chain of the fatty acid, the general chemical structure of FAME-biodiesel is then $R\text{-}COOCH_3$.

In recent works, the presence of nanostructures in ternary systems without conventional surfactants was reported [23–25]. The organisation of these nanostructures seems to be similar to those reported in classical microemulsions, where direct, bicontinuous and reverse structures can be found [26]. Other studies showed that this kind of nanostructure can be found in systems, where water is replaced by other hydrophilic solvents like glycerol, a deep eutectic or ethanol [27,28].

As the two main aims of the present work were the formulation of some ternary mixtures as biofuels and the determination of possible relations between the evolution of the kV and the temperature-dependent phase behaviour, following studies were performed:

(i) As the phase behaviour of ternary and binary systems is sensitive to temperature changes, it was investigated at 0, −15 and −20 °C.
(ii) The kV was measured for different compositions at 25 and 40 °C. Several standards exist across the world, giving a lower and upper value of the kV of petrodiesel or biodiesel fuel at 40 °C. For example, the standards ASTM D975 and EN 590 are used in the US and EU respectively for automotive petrodiesel. For automotive biodiesel, the standards ASTM D6751 and EN 14214 need to be fulfilled. In the present work, we especially checked if we can meet the standard ASTM D6751 for the kV and simultaneously obtain a clear and monophasic mixture. According to this standard, the kV of a biodiesel has to be between 1.9 and 6 mm^2/s.
(iii) Dynamic light scattering (DLS) measurements were performed to obtain information on the scattering intensities (SIs) of some of the ternary mixtures.
(iv) The critical points (CPs) of the systems using HepOH, ETBE, FAME and DMF as "ethanolotropes" were determined at 25 °C.
(v) The temperature dependence of some liquid/liquid mixtures close to the CP was investigated.
(vi) Concerning the system ethanol/HepOH/rapeseed oil, the results were analysed by using previously obtained small and wide angle X-ray scattering (SWAXS) and conductivity data [29].

2. Materials and methods

2.1. Materials

Ethanol (purity ⩾99.8%), tributyl citrate (⩾97%) and methyl tert-butyl ether (⩾99.8%) were purchased from Sigma-Aldrich GmbH (Steinheim, Germany). 1-Heptanol (⩾99%) and ethyl tert-butyl ether (⩾95%) were respectively purchased from Alfa Aesar